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(54) Improvement in concrete articles

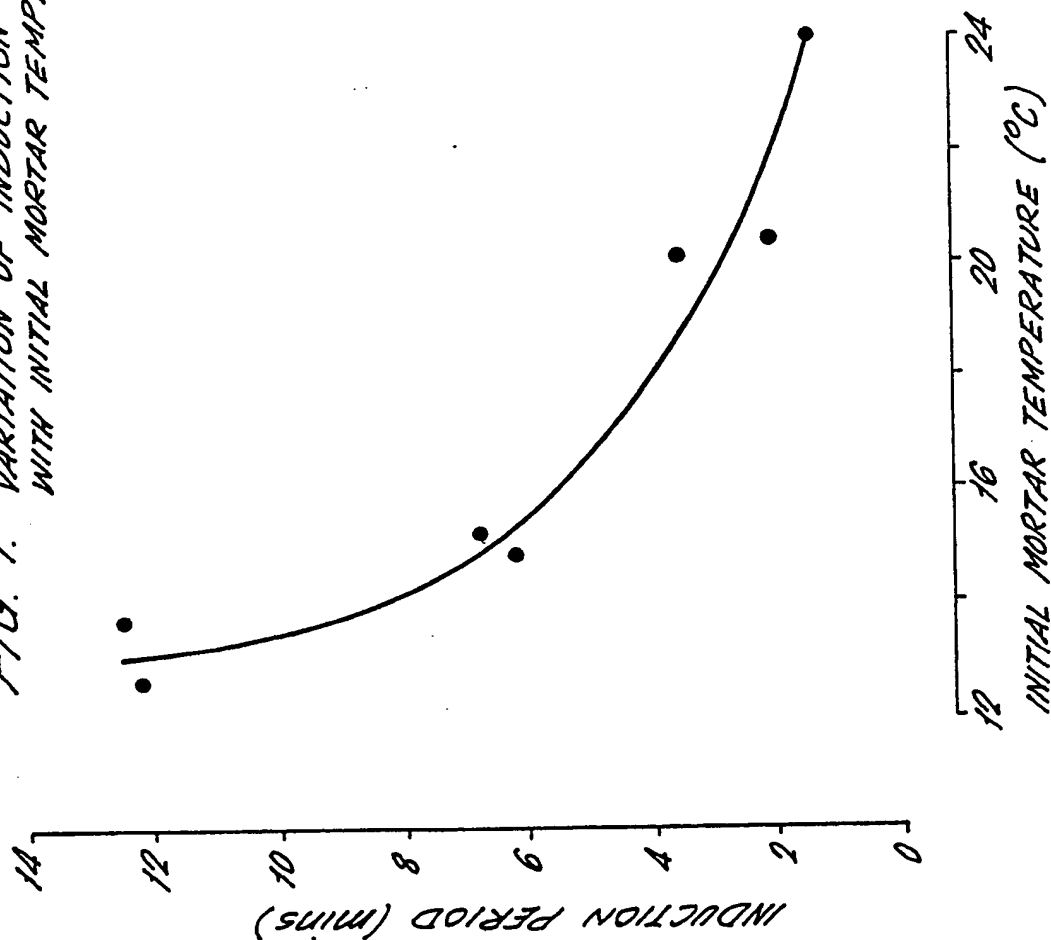
(57) A method of manufacturing concrete articles such as roof tiles wherein the void content of the fresh mortar is from 14 to 23% by volume also comprises the use of carbon dioxide or a carbon dioxide containing medium to accelerate the curing of the mortar.

Also provided is an apparatus for carrying out this method (Figs. 2, 3 not shown).

The drawing(s) originally filed was/were informal and the print here reproduced is taken from a later filed formal copy.

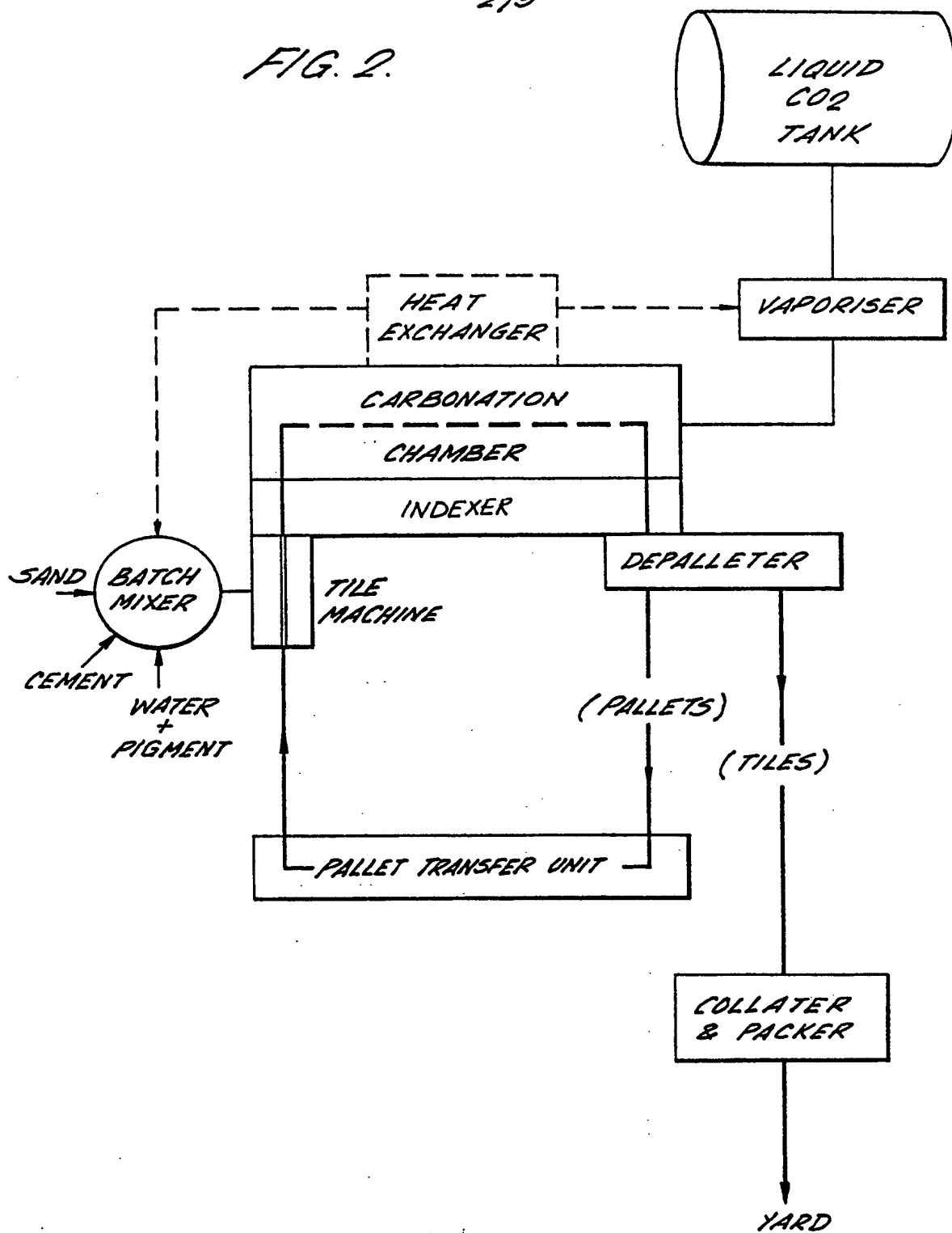
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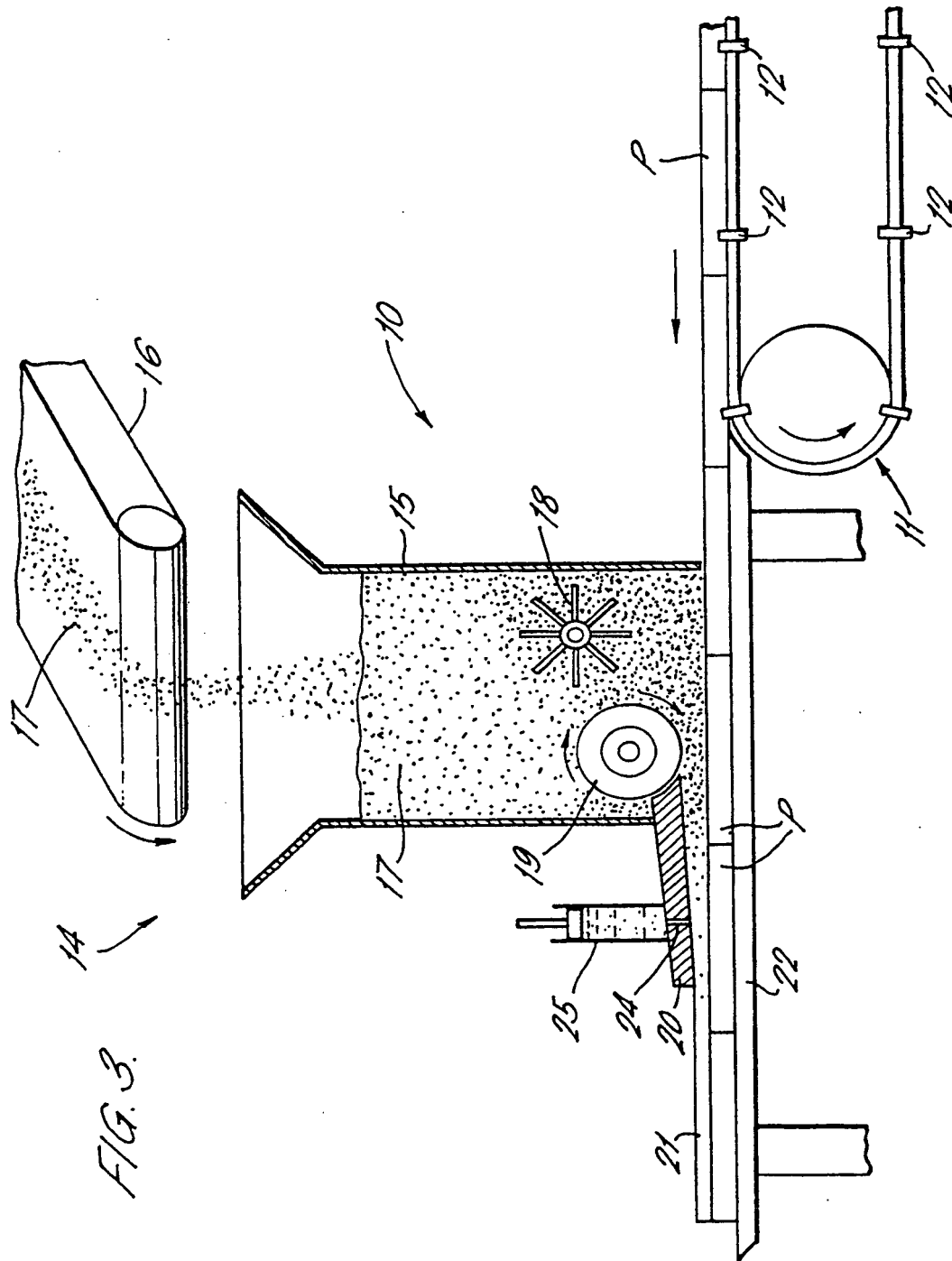
FIG. 1. VARIATION OF INDUCTION PERIOD
WITH INITIAL MORTAR TEMPERATURE.



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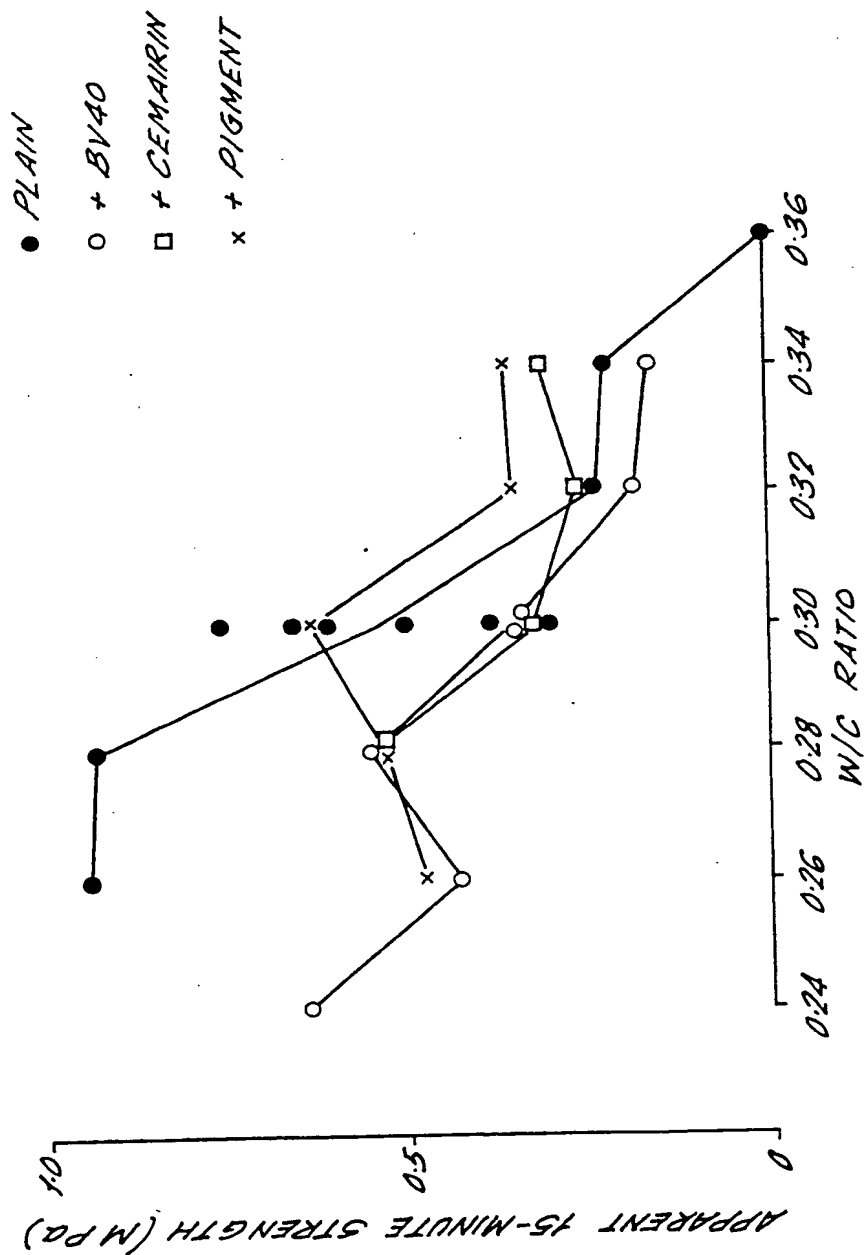
FIG. 2.





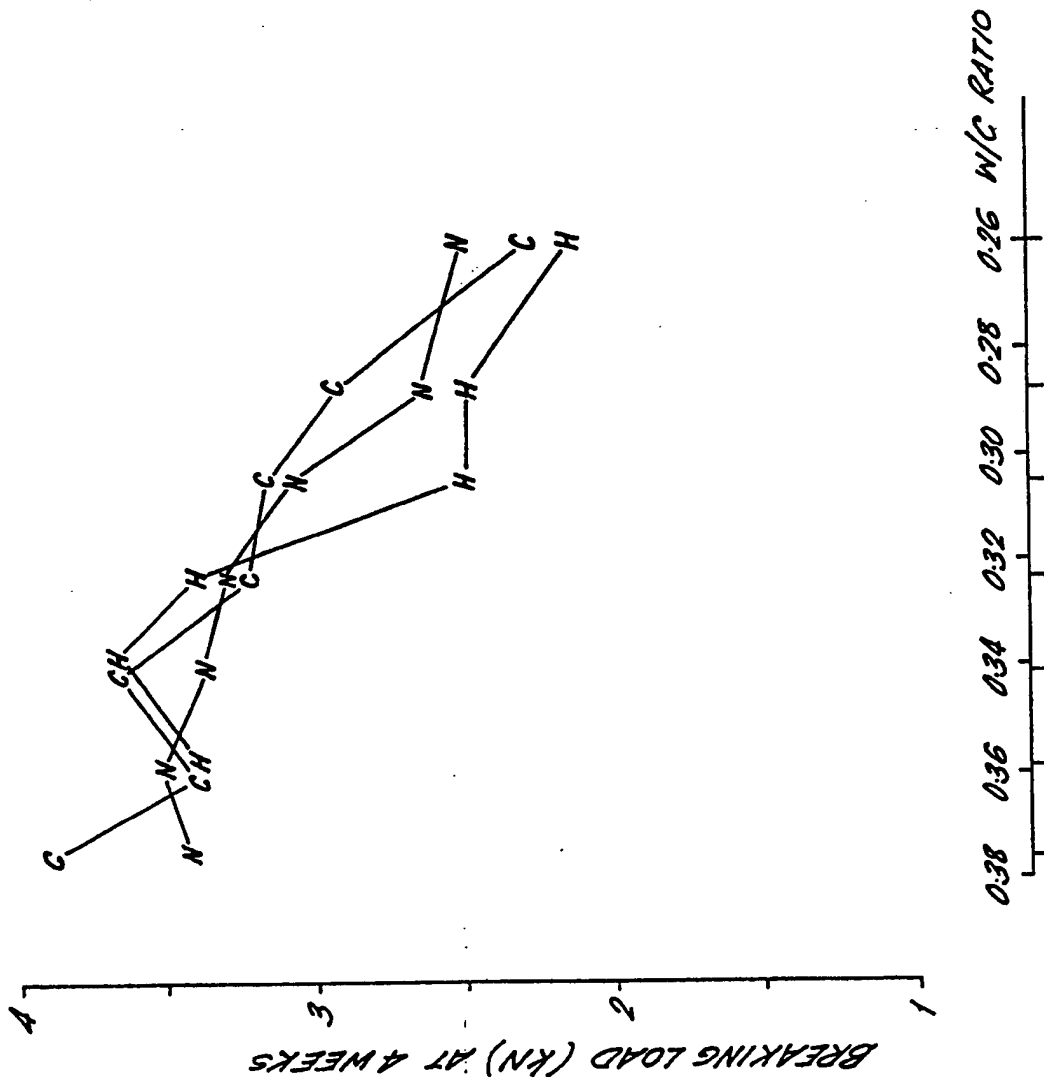
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FIG. 4. EFFECT OF W/C RATIO ON APPARENT STRENGTH AFTER 15 MINUTES CARBONATION.



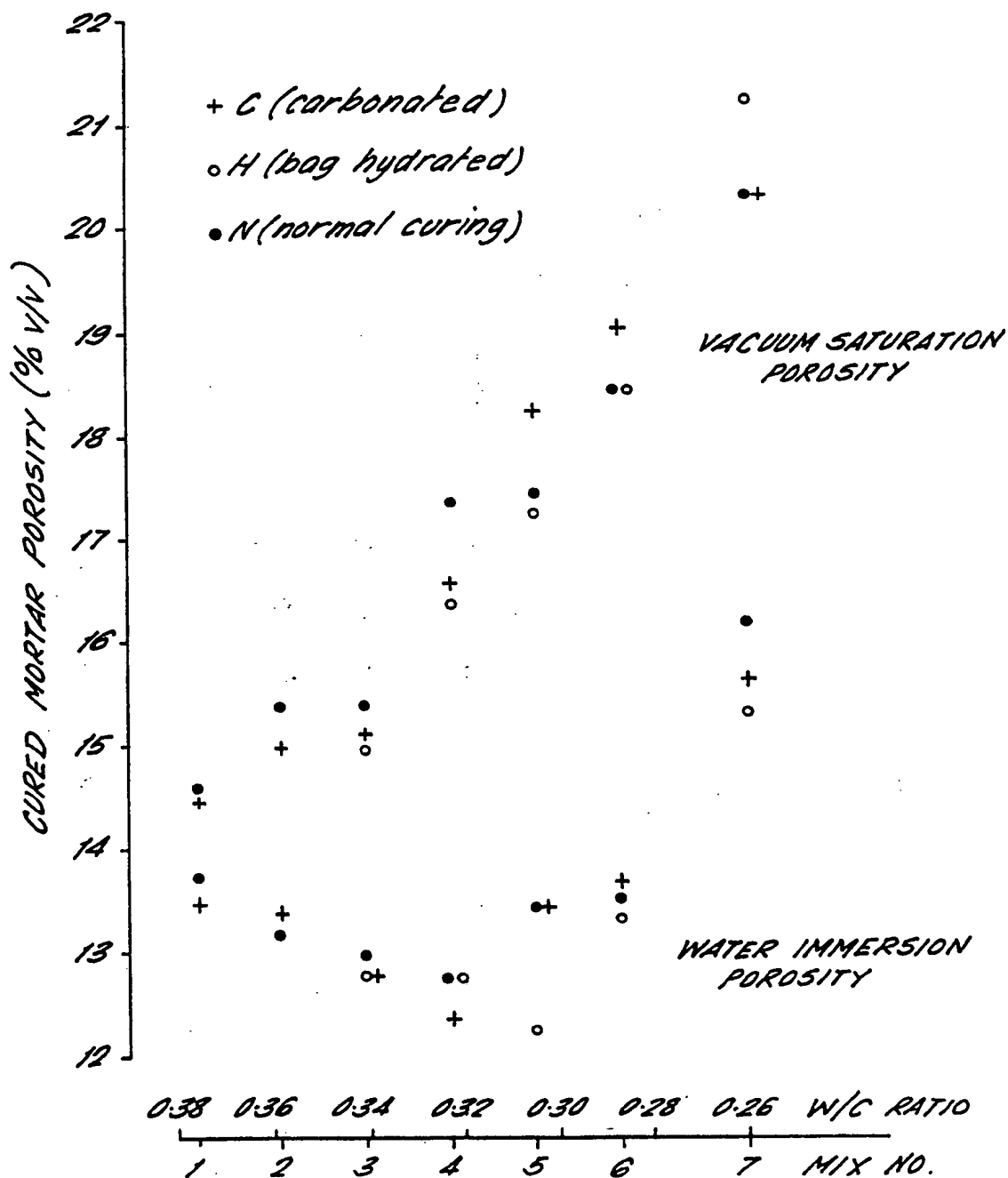
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FIG. 5. BREAKING LOADS AT 4-WEEKS VS W/C RATIO



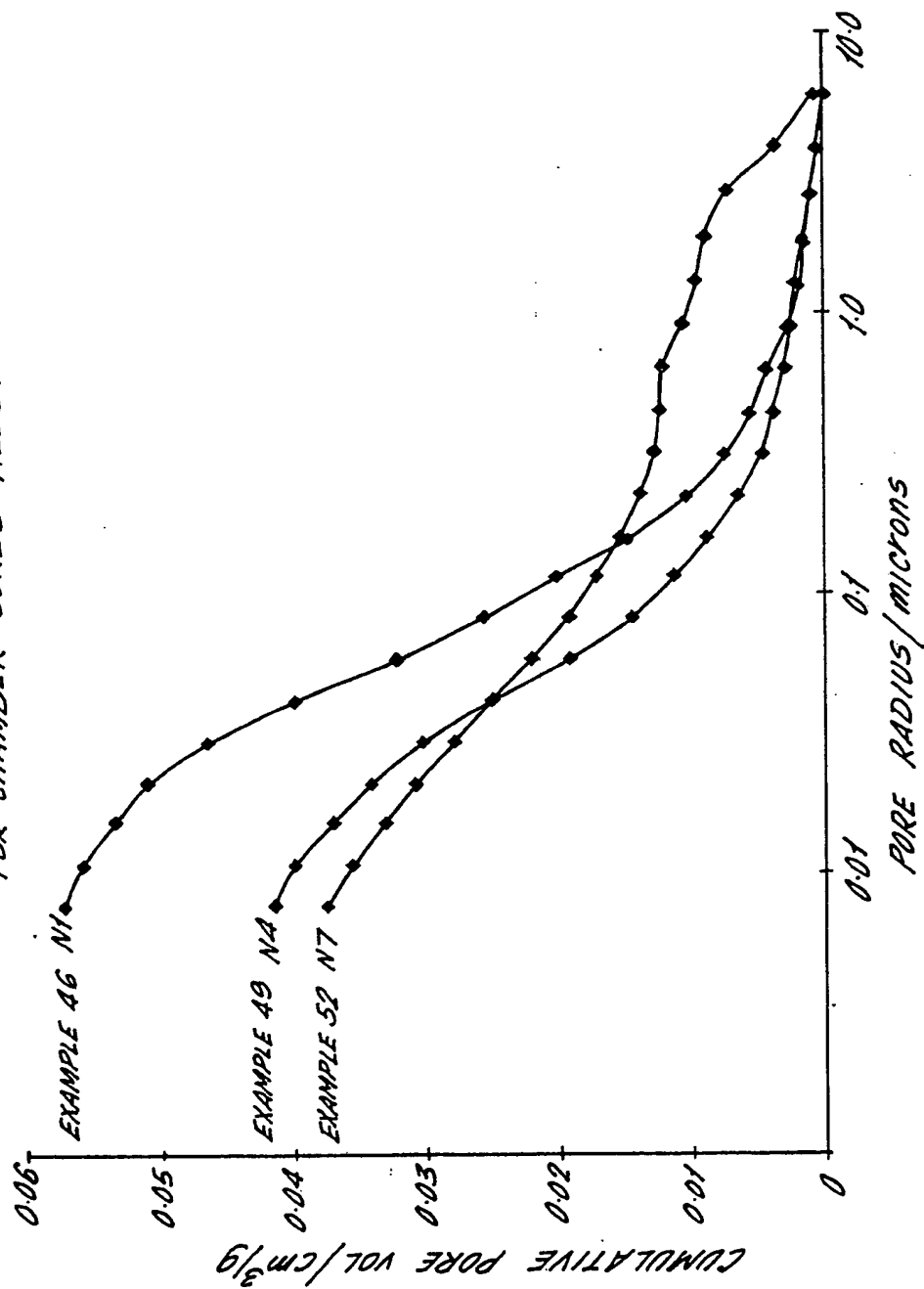
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FIG. 6. CURED MORTAR POROSITY vs W/C RATIO



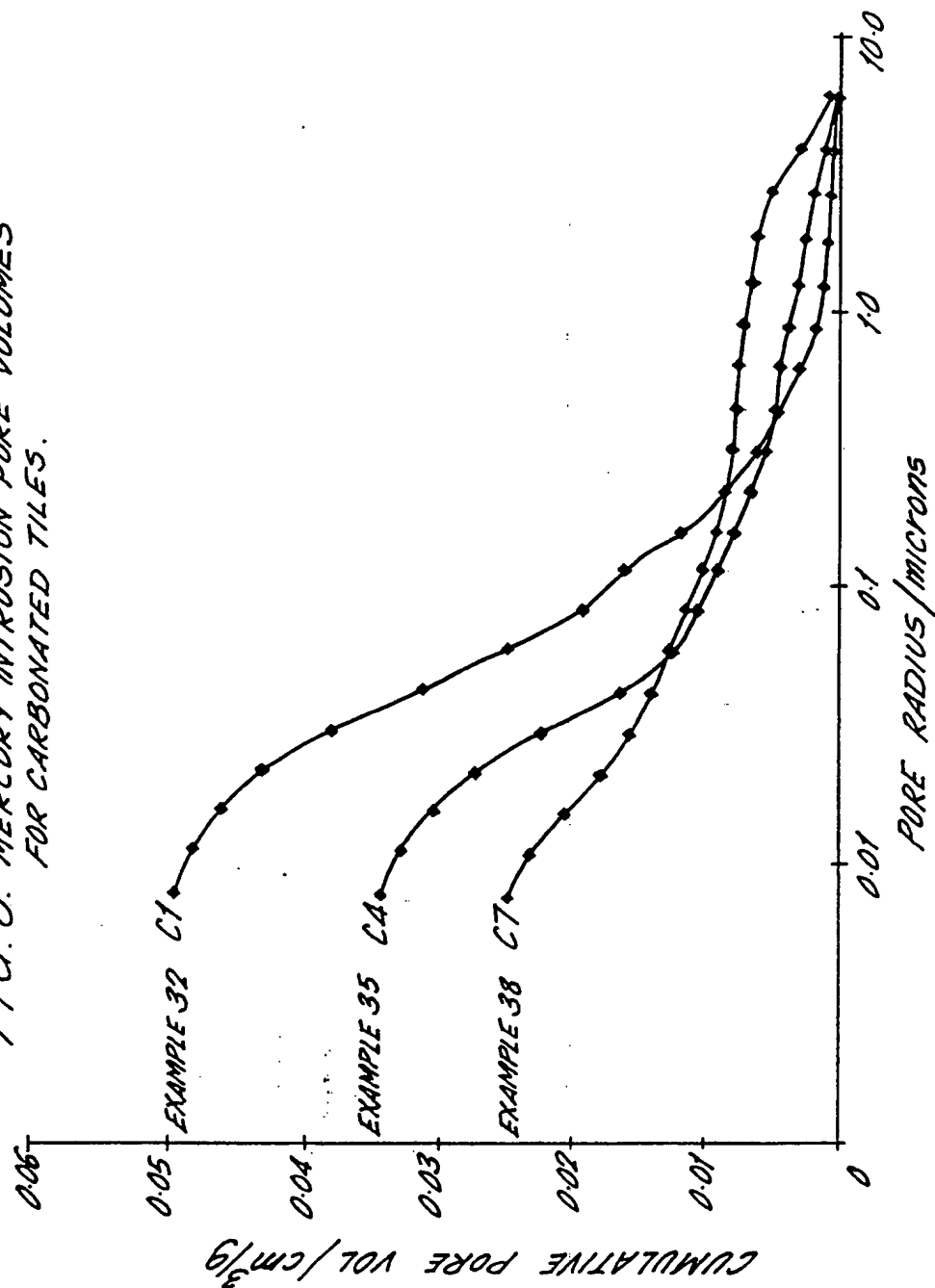
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FIG. 7. MERCURY INTRUSION PORE VOLUMES
FOR CHAMBER-CURED TILES.



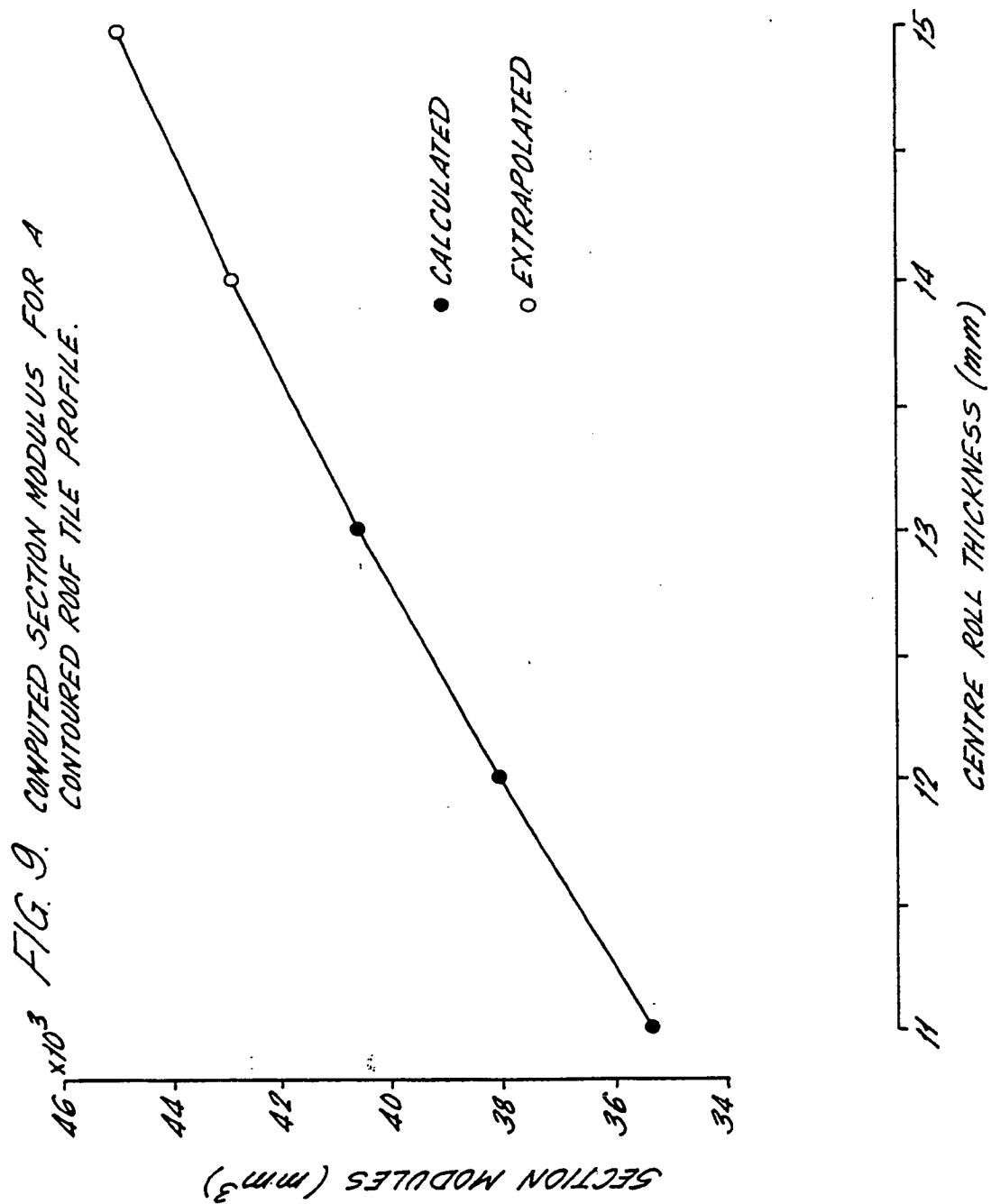
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FIG. 8. MERCURY INTRUSION PORE VOLUMES
FOR CARBONATED TILES.



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SPECIFICATION

Improvement in concrete articles

- 5 This invention is concerned with improvements in concrete articles and is particularly concerned with an improved method of manufacture of extruded concrete roof tiles, whereby their curing time is much reduced by carbonation, and an improved tile making machine for effecting said method. 5

10 The process and apparatus for the manufacture of concrete roof tiles are both well known. A relatively dry mortar mix of sand, cement and water usually in a ratio of about 3.5:1:0.4 is fed usually via a hopper and a shaping roller to form a continuous strip of mortar on a succession of pallets. The strip is subsequently cut at the junctions between the pallets to form individual green tiles, the green tiles on the pallets are cured and then the tiles are split from the pallets. 10

15 It will readily be appreciated that the requirement for pallets, in tile manufacturing methods where tiles are produced at up to 150 tiles per minute, together with the extensive storage space required for curing up to 100,000 tiles per shift, represents a very large investment. In addition, when one considers the maintenance required to keep the pallets and curing chamber in good working order, the initial outlay and ongoing costs for a tile producer are considerable. Thus, there are obvious advantages to be gained by: a) reducing the time that is required before a tile may be removed from its pallet without damaging the "green-state" product, and b) 20 obviating the need for extensive curing facilities. 20

Many proposals have previously been made for speeding up the curing of mortar mixes but so far none of these proposals has been capable of adoption in the manufacture of concrete roof tiles.

25 The use of carbon dioxide in the curing of mortar is well known but no process hitherto disclosed has been suitable for using in the manufacture of concrete roofing tiles where the quality and durability of the end products is to be ensured. 25

30 It is known to use carbon dioxide to harden concrete products, pre-cast tiles for example, which are self supporting before carbonation and which are removed from the mould before curing. Such processes are disclosed in, US 4093690, US 4117059 and US 4436498. US 4093690 and US 4117059 also disclose that the presence of 1-2% by weight of a vinyl acetate - dibutymaleate copolymer is required before the carbonation reaction will proceed. 30

35 US 3468993 also discloses the carbonation of self-supporting concrete products; here the products are carbonated after having been subjected to high pressure static compaction of at least 500psi and removed from their moulds. US 4117060 discloses the simultaneous compaction and carbonation of mortar within a mould. 35

US 4427610 discloses the curing of mortar by exposing the concrete shape, following compaction, to ultra-cold carbon dioxide to provide those shapes with early strength.

40 US 4069063 discloses the use of carbon dioxide added homogeneously to the cement slurry during the water-cement mixing stage in order to control setting of the cement and to stabilise the hydrated cement. 40

GB 1337014 discloses a process for producing concrete blocks involving presetting the blocks by injecting excess steam into the production zone and then by carbonating them.

45 GB 2106886-A discloses a method for the rapid hardening of concrete and similar materials by carbonation which involves the drying out of the capillary system of the concrete prior to and during carbonation. The drying process is a necessary feature of this invention and may be effected by a combination of air flow, heat generation and moisture absorption and, optionally, vacuum treatment. Also disclosed in this specification is a device designed for the carrying out of the method of the invention. 45

50 None of the prior art specifications discloses a process suitable for carbonating extruded roof tiles at atmospheric or only slightly supra-atmospheric pressured, nor do they disclose the carbonation of non-preset concrete products without earlier pre-carbonation steps. A study of the prior art moreover would suggest that additives such as the copolymers of US 4093690 and US 4117059 are necessary in order to carbonate concrete products successfully. 50

55 Our studies made in the course of the development of the present invention have surprisingly shown that products such as roof tiles can be readily carbonated by simple adaptations of the processing conditions and apparatus used hitherto. 55

60 We have now developed a method for the extrusion of concrete roof tiles which are not self supporting before carbonation but which, after carbonation, can be readily removed from their pallets without damage so that the pallets may be quickly reused. 60

65 In order to remove the roof tiles from the pallets shortly after production it is necessary for the tiles to be self supporting immediately after a fifteen minute curing process. This strength makes it possible to remove the tiles easily and without damage from the pallets and the fifteen minute time scale enables the pallets to be returned to the tile making machine quickly thus greatly reducing the number of pallets required and removing the requirement for extensive 65

curing facilities for soft tiles.

The present invention relates to a method of manufacturing concrete roof tiles which are self supporting after fifteen minutes curing.

Accordingly, the present invention provides a method of manufacturing concrete roof tiles wherein the void content (as hereinafter defined) of the fresh uncured mortar may conveniently be from 14 to 23% preferably from 18 to 23%, and more preferably from 19 to 21%, and where carbon dioxide or a carbon dioxide containing medium is used to accelerate the curing of the mortar. 5

The ratios of sand to cement to water that are required to produce mortars of the desired void content will vary with the different types of sand and cement that are suitable for the preparations of the mortars for the method of this invention. 10

Many different sands and cements as hereafter defined can be used to prepare the mortar.

In general however a water/cement ratio of from 0.15 to 0.32, preferably from 0.26 to 0.30, is required to produce fresh mortars having the desired void content.

The sand to cement ratio should generally lie in the range of from 2.5 to 4.5, preferably from 3.0 to 4.0. 15

While the high void content of the mortar and porosity of the tiles of the present invention is an advantage in that it permits rapid diffusion of carbon dioxide through the mortar in the carbonation stage it may also permit water to pass through the tile while it is in use. Water passes most readily through the larger pores while carbon dioxide will diffuse through much smaller pores; so in a preferred embodiment of the invention there is a restriction on the void size, preferably this will not exceed, in the fresh mortar 0.5mm, more preferably it will not exceed 0.2mm. 20

In order to ensure that carbon dioxide can permeate the mortar to carbonate it, the gas permeability of the fresh mortar should preferably exceed 10^{12} m/s. If the permeability is less than 2×10^{-13} m/s then the carbon dioxide will not be able to diffuse quickly through the mortar and carbonation will be very slow. On the other hand if the permeability is too great, the cohesion of the tile becomes reduced and the finished product is more open to water penetration. 25

Preferably the carbon dioxide is introduced to the fresh mortar at atmospheric pressure but it may be introduced at an elevated pressure of up to 5 atmospheres. The percentage of carbon dioxide in the carbonating atmosphere is preferably from 75% to 100%, more preferably 95% to 100%. In one preferred embodiment of the invention gaseous carbon dioxide is introduced to the mortar in an air tight chamber, which has been previously evacuated, so that air is excluded. 30

As the carbonation reaction proceeds more quickly at elevated temperatures, it is preferred to preheat the mortar to a temperature of from 10 to 40°C, more preferably of from 20 to 30°C. Fig. 1 shows the induction period (the difference in time from the introduction of carbon dioxide to the mortar to the commencement of the carbonation reaction) plotted against initial mortar temperature and shows clearly the effect of preheating the mortar. In one preferred arrangement the heat of the carbonation reaction is recycled to preheat the mortar. 35

In one arrangement the carbon dioxide is introduced to the mortar when the mortar is compacted on the pallets and preferably before the mortar is cut to provide individual tiles on the pallets. 40

A convenient way of introducing the carbon dioxide to the mortar is via appropriate apertures in the region of the slipper plate. 45

The pallets may be arranged to be permeable or may be provided with appropriate apertures allowing the passage of fluid emanating from the carbon dioxide containing medium.

An alternative would be for the carbon dioxide to be introduced into the mortar prior to the mortar being extruded. For example this could be done in the hopper.

It is to be understood that all the above references to carbon dioxide include the carbon dioxide in liquid, gas or solid form and also include carbon dioxide containing mediums such as carbonated liquids. 50

The invention also provides apparatus for making concrete roof tiles in which use is made of any of the above method steps.

There now follows descriptions of an embodiment of a suitable plant lay out and of an improved tile making machine according to the invention. These descriptions are to be read with reference to the accompanying Figs. 2 and 3 respectively. 55

One embodiment of a suitable plant lay out for the apparatus of the present invention is illustrated in Fig. 2. The sand, cement, water and additives such as pigment are mixed in the batch mixer, the mortar is then transferred to the tile machine where the tiles are shaped on the pallets, the tiles are then transferred via the indexer to the carbonation chamber to which carbon dioxide has been introduced via the vaporiser. The heat generated in the carbonated reaction is recycled by the heat exchanger to the batch mixer to preheat the mortar and to the vaporiser. Following carbonation the tiles on their pallets proceed via the indexer to the depalleter where they are separated, the pallets returning to the tile machine while the tiles proceed via the 60

collater and packer to the yard to mature.

An alternative embodiment of the invention is shown in Fig. 3; this is an illustration of the tile making machine where the carbon dioxide is introduced to the fresh mortar via an aperture in the slipper plate.

- 5 The machine 10, shown in the drawing, comprises a conveyor 11 of a conventional design, 5
having drive dogs 12 by which pallets P are fed seriatim through a tile machine station 14.

At the station 14, the machine 10 is provided with a mortar hopper 15 and a mortar conveyor 16, by which, when the machine is in use, the hopper is charged with concrete mortar 17.

- 10 The hopper 15 is provided with tined compaction device 18, a conventional compaction roller 19 and a slipper 20, which roller and slipper define, together with pallets P passing beneath the 10
hopper 15 when the machine is in use, a slit-like opening, through which mortar will pass to form a ribbon of mortar 22 on said pallets P.

- For supporting the pallets P, as they pass beneath the hopper as aforesaid, the machine 10 is 15
provided with a dead-bed 23 also of conventional design. . 15

The slipper 20 of the machine 10 is provided with an inlet 24 extending downwardly there-through, which inlet 24 is connected to a cylinder 25, fixedly mounted on the slipper 20.

- When the machine 10 is in use and tiles pallets P are conveyed beneath the hopper 15 as 20
aforesaid, by pressurising the cylinder 25, CO₂ in gaseous and/or liquid form is caused to pass 20
thorough said inlet 24 and into the mortar 17 via a porous plug (not shown) as it passes 20
underneath the slipper. The CO₂ is diffused throughout the mortar ribbon 21 to cause accelerated hydration thereof.

Immediately after exiting from the slipper, the ribbon of mortar 21 is cut by a knife, or knives, not shown, to form discrete green-state tiles on the pallets P

- 25 "Green-state" tiles formed as aforesaid and made from a mortar comprised of a 3.5:1.0:0.3 25
sand, OPC, water mixture were found to have a flexural strength of 1.9 MPa after 15 minutes. This early strength enables the separation of the "green-state" tiles from their respective pallets thereby releasing the pallets for subsequent tile making operations.

- Traditionally, tile pallets for the production of concrete roof tiles are made of metal and are 30
somewhat impervious by nature. It is envisaged that, in the present invention, pallets made from 30
a porous material will enhance the diffusion of the CO₂ gas through the tile mortar.

It is also foreseen that more than one inlet for CO₂ may be provided on the slipper along the length thereof and that inlets may also be provided in the check plates usually extending along the sides of the tile mortar adjacent to said slipper.

- 35 Obviously, the amount of CO₂ utilised will depend upon the mass and nature of mortar being 35
used to form the tiles and it is considered that the gas and/or liquid CO₂ may be fed to the various inlets at the same, or differential pressures, as required. Such a facility will be important where the cross section of the tiles being formed is not constant.

- If required, the "green-state" tiles may be subjected to further CO₂ treatment before, or after, 40
separation from their pallets P by passing them through a treatment chamber downstream of the 40
tile making station 14.

The invention is further illustrated with reference to the following Examples in which the sands and cements utilised have the sieve analyses and characteristics as shown in Tables A and B hereinafter.

- 45 The sands are basically quartz sands, i.e. they are high in silica content. 45

TABLE A

SAND CHARACTERISTICS

<u>DESIGNATION</u>	<u>SIEVE SIZES (Cumulative % Passing By Weight)</u>									
	<u>4.75</u>	<u>3.35</u>	<u>2.36</u>	<u>1.18</u>	<u>0.6</u>	<u>0.3</u>	<u>0.15</u>	<u>0.075</u>	<u>0.045</u>	<u>0.025</u>
A	100	98.9	91.5	65.7	16.0	1.6	5.5			
B	98.9	80.3	65.2	52.5	26.5	2.1	7.8			
C	99.2	93.7	87.2	75.8	57.9	18.7	2.8	4.7		
D	99.7	95.9	86.1	70.3	51.3	20.5	4.2	7.2		
E	100	99.2	93.6	64.8	14.4	2.2	14.7			

TABLE B
CEMENT CHARACTERISTICS

Designation	F	G	H	I	J	K
CHARACTERISTICS						
Specific surface area (m ² /kg)	346	378	362	303	466	486
Oxide analysis (%)						
- SiO ₂	21.0	19.8	19.4	19.3	19.6	20.1
- Al ₂ O ₃	4.2	5.4	5.2	5.2	5.1	5.0
- Fe ₂ O ₃	1.9	2.5	3.0	3.0	2.9	2.4
- CaO	65.3	64.0	65.2	64.7	64.8	65.6
- MgO	1.0	1.3	1.3	1.2	1.2	0.9
- SO ₃	2.5	2.9	2.8	3.3	3.2	2.4
- K ₂ O	0.61	0.8	0.65	0.75	0.68	0.71
- Na ₂ O	0.14	0.2	0.17	0.17	0.15	0.10
- Loss on ignition	1.9	2.4	1.5	1.6	1.6	1.4
- free lime	2.1	1.2	0.6	0.6	0.7	1.1
Lime saturation factor	97.7	97.5	101.2	100.3	99.5	100.1
Bogue compound composition(%)						
- C ₃ S	59.6	61.9	68.3	65.6	64.5	66.0
- C ₂ S	15.2	10.1	4.1	5.8	7.6	7.9
- C ₃ A	7.9	10.1	8.7	8.7	8.6	9.2
- C ₄ AF	5.8	7.6	9.1	9.1	8.8	7.3
Initial set (mins)	195		130	150	85	80
Final set (mins)	265		205	215	145	140
Standard consistency (%)	26.3		26.3	25.5	26.5	25.5

The data in Table B above were obtained by the methods outlined in British Standards No. 12:1978 (Ordinary and rapid-hardening Portland Cement) and No. 4550:1978 (Methods of Testing Cement) with the exception of the Bogue compound compositions which were calculated according to the formulae given in A.S.T.M. Standard C 150-85 (Portland Cement)

EXAMPLES 1-29

Tiles were prepared from cements, sands and water in the proportions set out in Table 1 with the optional addition of red oxide pigment (Deanshanger 'L12'), plasticiser (Sika 'Plastiment - BV40') or air-entrainer (Cementation Chemicals 'Cemairin').

- 5 Sand and cement were mixed dry in an Eirich Pan mixer together with any additives for 1 minute, the sand/cement ratio being a constant 3.5. Water was then added in the water/cement ratios listed in column 2 of Table 1, and the mixture was mixed for a further 3 minutes. 5

- 10 The tile machine was an ordinary commercial tile making machine used under laboratory conditions although it was used in its standard settings, i.e., the ones normally used for tile commercial production. The tile machine hopper was filled with mortar which was compacted under the slipper by running the roller on its own for a few seconds to ensure that the first few tiles of each run (corresponding to one mortar batch) were of reasonable quality. Four tiles were selected from each run and two were subjected to accelerated carbonation, while the other two were bag cured for 24 hours. 10

- 15 The accelerated carbonation procedure involved the placing of the two tiles on their pallets in a plastic bag (55×88cm) which was inflated by injecting CO₂ (from a liquid cylinder via a vaporiser at rates up to 30 litre/minute) to maintain a slight positive pressure for fifteen minutes. The mortar temperature was monitored throughout the fifteen minutes by means of a thermo-couple probe. 15

- 20 Various properties of the fresh mortar and of the carbonated tiles were investigated. Of the newly carbonated tiles, the strength (columns 7 and 9 of Table 1), the surface appearance (column 10) the Ridsdale weight (column 11), of the fresh mortar the percentage of the voids (column 12), and of the cured mortar porosity (column 13), were measured. 20

Measurements of these properties were carried out as described below.

- 25 *Strength Testing* 25

- The strengths of both carbonated specimens of each example were determined as soon as possible after carbonation by means of 3-point transverse loading. For breaking loads below 200N, tiles were tested using the Salter Force Gauge mounted on a drill stand, adapted to load transversely on bearer rods 350mm apart with a central load bar resting on the two rolls of the tile. 30

When breaking loads exceeded 200N, tiles were tested at a span of 280mm on a B.S. tile breaker. Such tile breakers give breaking loads which are about 15% higher than those given by an Instron '1116' Universal Testing Machine.

- 35 Transverse breaking loads have been converted into apparent mortar bend strengths by means of the formula 35

$$W.S$$

- 40 $P = 4z$ 40

where P is the strength in MPa

W is the breaking load in N

S is the bearer span in mm

- 45 and z is the section modulus in mm³. 45

Values of z, computed for a contoured tile with a range of centre roll thicknesses, are plotted in Fig. 9. The 'apparent' strength thus calculated assumes that the load is applied 'ideally' (i.e. distributed to avoid stress concentration), but it has been found in practice that 'real' strengths measured in the tile mortar may be up to 50% higher than 'apparent' strengths obtained from tile-breaker loads. 50

Apparent strengths were calculated from the mean of two breaking loads. Because of the difficulty in ensuring complete removal of air from the bag prior to carbonation, one tile always appeared to be less well carbonated and therefore weaker than the other, so that quoted mean strength is probably an underestimate of what could be achieved with a better engineered carbonating system. 55

Surface Appearance

Surface appearance was rated by Comparison with non-carbonated tiles on the following scale:

5—excellent

- 60 4—good 60

3—acceptable

2—poor

1—very poor.

Ridsdale Weight

- 65 The Ridsdale weight is defined as the weight of a block of mortar of 188cm³ which has been 65

rammed to that constant volume.

Percentage of Voids in Fresh Mortar

The Fresh Mortar Void content is defined as

$$5 \quad E(\%) = 100(1 - D/D_0)$$

where D is the mortar density as measured on a cylinder of mortar rammed to constant volume on a Ridsdale sand Rammer and D_0 is the theoretical void free mortar density defined as

$$D_0 = A + 1 + W / \{A/P_s + 1/P_c + W\}$$

10 for an aggregate: cement: water ratio of A:1:W and for aggregate and cement densities of P_s and P_c respectively.

Cured Mortar Porosity

The cured mortar porosity is measured by the normal water saturation method.

15 Examples 1–6 illustrate the effect of reducing the water/cement ratio while keeping other variables constant for a Sand "D"/cement "F" mixture. Examples 7–10 illustrate the same effect when Cemairin air-entrainer is added to the mixture, examples 11–16 when BV40 plasticiser is added and Examples 17–20 when pigment 5 red oxide pigment is added. Examples 22–25 illustrate the effects of using different sands at a constant sand/cement ratio of 0.30, and examples 26–29 show the effects of using different cements.

Maximum apparent strength after 15 minutes is achieved at low or intermediate water/cement ratios. The apparent strength is plotted against w/c ratio in Fig. 4.

25 The carbonation process is tolerant of a wide range of sands, but Sands "D", "A" and "C" give the highest 15 minute strengths; in general the mortars with the highest void content produce the highest 15 minute strengths. Similarly the process is tolerant of a range of cements with cements "G" and "F" giving the highest 15 minutes strengths.

30 The addition of pigment, plasticiser or air-entrainer tends to slightly reduce both mortar void content and fifteen minute strength but not by any significant amount. That the addition of air-entrainer should decrease void content may indicate that its plasticising characteristics predominate at the comparatively high ramming pressures used.

The monitoring of mortar temperature during the carbonation showed that it would be possible to increase the temperature of mortar, pallets and other apparatus to a temperature of at least 20°C at which the carbonation reaction may proceed more quickly.

35 **EXAMPLE 30**

The procedure of the earlier examples was repeated except that the aggregate/cement/water ratio was 4.5/1/0.3. The results are tabulated in Table I, cement "F" and sand "D" were used, no additives were added. The effect on 15 minute strength was not great, nor was the effect on porosity, of changing the aggregate/cement ratio.

40 **EXAMPLES 31–51**

In these examples the investigations undertaken for the tiles of examples 1–30 were continued and extended under actual works conditions rather than under laboratory conditions. Comparisons between carbonated tiles (examples 31–37), bag hydrated tiles (examples 38–44) and 45 chamber cured tiles (examples 45–51) were carried out.

The tiles were prepared from the cements, sands, water and admixture in the proportions set out in Table 2. Sand "E" and cement "K" were used, the pigment was a commercially available iron oxide pigment. The tiles were prepared using an ordinary commercial tile machine in its standard settings.

50 Following manufacture of the tiles, of the tiles from each mix, 4 were carbonated, 2 were bag cured and 8 were chamber cured. When more than one tile was tested to ascertain a particular property an averaged result is quoted.

55 The carbonated tiles were carbonated by the process described in examples 1–30 and are designated C. The bag cured tiles, designated H, were sealed on their pallets in polythene bags and left to hydrate at ambient temperature (between 5 and 15°C) for 48 hours. The chamber cured tiles were subjected to the normal chamber curing cycle, and are designated N.

60 The strength of the depalletable carbonated tiles was measured after 15 minutes carbonation. The tiles of Examples 31–37 are prepared for mixes 1–7 of Table 2. Their strength was measured using three-point flexure on parallel bearer rods 350 mm apart, with a central bar resting on the two rolls of the tile loaded by means of a Salter Force Gauge mounted on a drill stand.

65 Example 31 prepared from the mortar from Mix 1 showed no change after carbonation, and tiles were therefore not depalletable. Example 32, tiles from Mix 2, had developed a slight surface crust, especially on the locks where the mortar is less well compacted, but were still not depalletable. The surface crust was more evident in Example 33 prepared from Mix 3, but only

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with Example 34 (Mix 4) had sufficient strength been developed for tiles to be depalleted: unfortunately they were not quite strong enough to support their own weight and could therefore not be tested for strength. Tiles from the remaining mixes (examples 35–39) were all easily depalletable and yielded strengths which increased with reduction in w/c ratio, and in some cases exceeded the capacity of the Force Gauge (200N).

The 15 minute strengths thus measured are listed in the final column of Table 2. None of the bag or chamber cured tiles could be depalleted after this short curing time.

The fact that the strengths of the carbonated tiles were lower than the strengths measured in examples 1–29 for similar w/c ratios is due to the fact that the carbonation reaction can proceed to a lesser extent in the tiles of the present examples which have been more highly compressed by the works-tuned tile manufacturing machine.

The properties of the cured and matured tile samples were measured and the results obtained as described below.

15 *Flexural strength*

After storing dry for 4 weeks, breaking loads were measured on dry tiles in 3-point flexure, using parallel bar breakers mounted at a span of 280mm in a model 1116 Instron running at a cross-head speed of 0.5mm/minute.

The measured breaking loads are shown in Table 3: where more than one tile of a type was tested, a standard deviation is given, together with the number of tiles tested in brackets. These results are plotted against w/c ratio in Fig. 5. There is little difference in strength between the three curing regimes at any of the mix w/c ratios, but reducing the w/c ratio from 0.38 to 0.26 causes the flexural strength to fall by more than 30%.

25 *Density and porosity of water immersion*

Densities were measured, in triplicate, on samples about 5cm square cut from the valleys of the tiles. Two methods were used: the normal water immersion method and the more recently developed technique of vacuum saturation, where the specimens are placed in water under vacuum for 24 hours instead of merely being soaked in an open tank for 24 hours.

'Wet' (saturated and surface dry) and oven dry densities, determined densities, determined by water immersion, are tabulated for each mix in Table 4, which shows that there is a little difference between chamber cured (N), bag hydrated (H) and carbonated (C) densities at each w/c ratio. There is little fall in density with reduction in w/c ratio until the last two mixes.

Porosities determined by the two techniques are tabulated in Table 5 and plotted as a function of w/c ratio in Fig. 6. The values (numerically equal to the difference between wet and dry densities, expressed as a percentage) represent the void space which is accessible to water, and are less sensitive to the curing regime than to the original water content of the mortar mix.

Whereas the 'vacuum saturated porosity' increased steadily with falling w/c ratio, the water immersed porosity reached a minimum at a w/c ratio of about 0.32. Since vacuum saturation enables smaller pores to be filled by water, this suggests that the initial effect of w/c reduction (0.38 to 0.32) is to increase the number of small pores, and that the number of larger pores does not begin to increase until the w/c ratio falls below 0.32.

Porosity by mercury intrusion

Selected specimens from Mix Nos. 1, 4 and 7; either carbonated or chamber cured (i.e. examples 31, 34, 37, 45, 48 and 51) were examined by mercury intrusion porosimetry (MIP), which measured pore volumes in the size range 0.005 to 7.5µm.

The results of determinations in duplicate are presented in Figs. 7 and 8, where the cumulative pore volume (in cm³/g) is plotted against the pore radius. These distributions show that the porosity in this size range, and especially below 1µm, actually falls with decreasing w/c ratio, in contrast to the results from water immersion testing. This is consistent with the known effect of w/c ratio on the capillary space within hardened cement paste.

Carbonated tiles had a slightly lower porosity than chamber cured, presumably because deposition of calcium carbonate during carbonation blocks the finer pores.

Mortar microstructure

6 tile samples of the same tiles that were used for measuring mercury intrusion i.e. Examples 31, 34, 37, 45, 48 and 51 have been examined by back-scattered electron imaging (BSEI). This technique produces an image on the electron microscope whose contrast varies with the atomic number density of the phases present, and can thus distinguish easily between pores, cement paste and aggregates in mortar. In addition, it is possible to feed the electron image into a versatile multi-colour image analyser which enhances the contrast and can quantify the proportions of phases present and perform statistical operations on them.

Before polishing to a flat surface with 1µm diamond paste, specimens were impregnated with polymer to enhance the contrast of the pores. It was estimated that the magnification used

($\times 100$), the image analysing system was capable of resolution down to about $50\mu\text{m}$.

The relative volumes of phases present in mortars, obtained from averaging 4 or more fields for each specimen, are shown in Table 6.

- 5 As expected, porosity increased with reduction in w/c ratio from mixes 1 to 4 to 7, and there was little difference between carbonated and chamber cured specimens or between roll and valley sections. The porosity of examples 31 and 45 was considerably less than that measured by water immersion, probably because the more viscous resin was less able to penetrate the smaller pores. 5

10 *Pore size distribution* 10

Electron microscopy of tile sections (see above) has suggested that lowering the w/c ratio of tile mortar may affect both the spatial and size distribution of porosity. Volume porosities determined by different techniques are compared in Table 7. The pore size range covered by mercury intrusion (MIP) is related to the pressure used and the contact angle of mercury: the ranges for water immersion and vacuum saturation have been estimated assuming that water will penetrate all the capillary (but not gel) pores in the cement paste under vacuum, but will not reach the smaller capillary pores if no vacuum is applied. 15

The data in Table 7 shows that with decreasing w/c ratio

- 20 (i) porosity below $1\mu\text{m}$ (MIP) falls
(ii) porosity between 1 and $7.5\mu\text{m}$ (MIP) rises 20
(iii) the 'total' porosity (water under vacuum) rises
(iv) the smaller water-accessible porosity (difference between vacuum saturation and immersion) rises.

- 25 This last observation conflicts with the first, suggesting that the type or shape of pores penetrated by mercury and water may be different. Nevertheless, comparison of the mercury and water pore volumes indicates that the large porosity (greater than a few μm) increases considerably with decreasing w/c ratio. 25

TABLE 1
Summary of Run Parameters

Examplos Ratio	Cement if not Cement "F"	Sand Sand "D"	Additive (Dosage w/w cement) (%)	Tile Wt. (g)	Mean Load Thick- (N) ness	Apparent 15 minute (MPa)	Surface Appearance (1-5)	Riddale weight (g)	Estimated voids(%) in Fresh mortar	Cured porosity (%)
1	0.36			4959	101	-	3	374	18.1	17.1
2	0.34			4960	108	0.21	3	382	16.8	16.8
3	0.32			4960	108	0.22	3	380	17.8	16.8
4	0.30			4904	460	0.75	3	370	20.4	16.7
5	0.28			4650	555	0.92	3	365	22.0	16.9
6	0.26			4667	557	0.93	2	365	22.5	17.0
7	0.34		Cemalrin 0.12	4717	145	0.30	3	385	16.2	-
8	0.32		Cemalrin 0.12	4625	124	0.25	3	-	-	-
9	0.30		Cemalrin 0.12	4628	166	0.32	3	385	17.2	-
10	0.28		Cemalrin 0.12	4628	320	0.53	4	-	-	-
11	0.34		BV40 0.5	4973	752	0.16	4	381	17.0	18.8
12	0.32		BV40 0.5	5070	87	0.18	5	379	18.0	18.8
13	0.30		BV40 0.5	4958	201	0.33	3	379	18.5	19.5
14	0.28		BV40 0.5	4934	340	0.55	3	375	19.8	19.9
15	0.26		BV40 0.5	4475	260	0.43	2	369	21.6	-
16	0.24		BV40 0.5	4610	380	0.64	4	366	22.7	-
17	0.34		Pigment 5	4792	215	0.36	3	-	-	20.1
18	0.32		Pigment 5	4797	210	0.35	1	381	17.6	20.7
19	0.30		Pigment 5	4840	380	0.64	4	369	20.6	-
20	0.28		Pigment 5	4701	310	0.53	2	365	22.0	21.8
21	0.26		Pigment 5	4451	280	0.48	2	-	-	21.6
22	0.30	"A"		4709	325	0.55	4	390	16.1	-
23	0.30	"E"		4829	105	0.23	5	398	14.4	-
24	0.30	"C"		4851	179	0.39	4	387	16.8	-
25	0.30	"B"		4790	64	0.13	2	387	16.8	-
26	0.30	"G"		4788	395	0.66	3	373	19.8	-
27	0.30	"H"		4677	208	0.36	2	-	-	-
28	0.30	"I"		4582	210	0.34	3	-	-	-
29	0.30	"J"		4664	210	0.36	2	-	-	-
30	0.30	"D"		4650	305	0.51	2	362	22.1	20.5

at 4.5 a/c

TABLE 3 Breaking loads for tiles tested at an age of 4 weeks

5	CURING REGIME				5
10	MIX	(EXAMPLES 45-51) N	(EXAMPLES 38-44) H	(EXAMPLES 31-37) C	10
15	1	3410+190(4)	-	3900	15
	2	3460+260(4)	3400	3400	
	3	3350+280(4)	3650	3630+40(2)	
20	4	3260+540(4)	3380+250(2)	3200	20
	5	3060+280(4)	2450	3100	
	6	2590+190(4)	2450	2910+420(4)	
25	7	2440+100(4)	2100	2260+430(5)	25

TABLE 4 'Wet' (saturated and surface dry) and oven dry densities determined by water immersion (means of 3 samples).

35								35
		Wet density			Dry density			
40	Example No.	(45-51)	(38-44)	(31-37)	(45-51)	(38-44)	(31-37)	40
		N	H	C	N	H	C	
	Mix No.							
	1	2.336	-	2.319	2.198	-	2.184	
45	2	2.340	-	2.368	2.207	-	2.233	45
	3	2.340	2.330	2.339	2.210	2.202	2.210	
	4	2.345	2.347	2.300	2.216	2.219	2.176	
50	5	2.321	2.329	2.341	2.186	2.206	2.206	50
	6	2.315	2.332	2.309	2.179	2.198	2.172	
	7	2.294	2.248	2.294	2.131	2.094	2.137	
55								55

TABLE 5 Porosities determined by water immersion and by vacuum saturation

Example No.	Water immersion porosity (%)			Vacuum saturation porosity (%)		
	(45-51)	(38-44)	(31-37)	(45-51)	(38-44)	(31-37)
Mix No.	N	H	C	N	H	C
1	13.7	-	13.5	14.6	-	14.5
2	13.2	-	13.4	15.4	-	15.0
3	13.0	12.8	12.8	15.4	15.0	15.1
4	12.8	12.8	12.4	17.4	16.4	16.6
5	13.5	12.3	13.5	17.5	17.3	18.3
6	13.6	13.4	13.7	18.5	18.5	19.1
7	16.3	15.4	15.7	20.4	21.3	20.4

TABLE 6 Relative volumes of phases in tile mortars, determined by back-scattered electron imaging.

Example No.	31	31	34	34	37	45	48	51
	Roll	Valley	Roll	Valley				
Volume %								
Pores	6	6	15	13	15	8	13	16
Sand	70	72	63	66	66	75	66	63
Hydrates	21	18	17	17	15	14	16	16
Clinker	3	4	5	4	4	4	5	5

TABLE 7 Porosities (volume %) determined by mercury intrusion, water immersion and vacuum saturation

Technique	Mercury porosimetry		Water immersion		Vacuum saturation
	Size range	Max. 1 μ m Min. 5nm	7.5 μ m 1 μ m	mm μ m	mm nm
Example No.					
45		12.2	0.6	13.9	16.0
48		9.2	0.6	13.0	17.3
51		5.1	2.6	16.7	21.0
31		10.9	0.3	13.0	16.9
34		6.7	0.9	15.2	18.6
37		4.1	1.6	15.0	21.3

CLAIMS

1. A method of manufacturing concrete articles wherein the void content (as hereinbefore defined) of the fresh mortar is from 14 to 23% by volume and wherein carbon dioxide or a carbon dioxide containing medium is used to accelerate the curing of the mortar.
2. A method as claimed in Claim 1 wherein the void content of the fresh mortar is from 18 to 23% by volume.
3. A method as claimed in claim 2 wherein the void content of the fresh mortar is from 19 to 21% by volume.
4. A method as claimed in any one of the preceding claims wherein the water to cement ratio of the fresh mortar is in the range of from 0.15 to 0.32.
5. A method as claimed in Claim 4 wherein the water to cement ratio is in the range of from 0.26 to 0.30.
6. A method as claimed in any one of the preceding claims wherein the sand to cement ratio of the fresh mortar is in the range of from 2.5 to 4.5.
7. A method as claimed in Claim 6 wherein the sand to cement ratio is in the range of from 3.0 to 4.0.
8. A method as claimed in any one of the preceding claims wherein the largest pore size in the fresh mortar is 0.5mm.
9. A method as claimed in Claim 8 wherein the largest pore size in the fresh mortar is 0.2mm.
10. A method as claimed in any one of the preceding claims wherein the gas permeability of the fresh mortar is at least 2×10^{-13} m/s.
11. A method as claimed in Claim 10 wherein the gas permeability of the fresh mortar is at least 10^{-12} m/s.
12. A method as claimed in any one of the preceding claims wherein the carbon dioxide or carbon dioxide containing medium is used to accelerate curing at a pressure in the range of from 1 to 5 atmospheres.
13. A method as claimed in Claim 12 wherein the pressure is 1 atmosphere.
14. A method as claimed in any one of the preceding claims wherein the percentage of carbon dioxide in the carbonating atmosphere is from 75% to 100%.
15. A method as claimed in Claim 14 wherein the percentage of carbon dioxide in the carbonating atmosphere is from 95% to 100%.
16. A method as claimed in any one of the preceding claims wherein the mortar is preheated to a temperature of from 10 to 40°C before carbonation.

17. A method as claimed in Claim 16 wherein the mortar is preheated to a temperature of from 20 to 30°C before carbonation.
18. A method as claimed in Claims 16 or 17 wherein the heat of the carbonation reaction is used to preheat the mortar.
- 5 19. A method as claimed in any one of the preceding claims wherein the carbon dioxide or carbon dioxide containing medium is introduced to the mortar on the pallets, preferably before it is cut to provided individual tiles. 5
20. A method as claimed in Claim 19 in which carbon dioxide is introduced to the mortar via appropriate apertures in the slipper plate.
- 10 21. A method as claimed in any one of Claims 1 to 19 wherein the pallets are permeable or are provided with appropriate apertures for the flow of fluid emanating from the carbon dioxide containing medium. 10
22. A method as claimed in any one of claims 1 to 18 wherein the carbon dioxide is introduced into the mortar prior to the mortar being compacted (e.g. on the hopper).
- 15 23. A method of manufacturing concrete roof tiles as claimed in any one of the preceding claims and substantially as hereinbefore described with reference to the examples. 15
24. Apparatus for carrying out the method as claimed in any one of claims 1 to 23 or substantially as hereinbefore described with reference to the drawings.
25. A concrete roof tile produced by a method as claimed in any of claims 1 to 23.
- 20 26. A roof comprising a plurality of tiles as claimed in claim 25. 20

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